

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2008-179830

(43)Date of publication of application : 07.08.2008

(51)Int.Cl.

COBL 101/10 (2006. 01)
COBL 71/02 (2006. 01)
COBK 5/098 (2006. 01)
COBK 5/17 (2006. 01)
COBL 23/26 (2006. 01)

(21)Application number : 2008-068519

(71)Applicant : KANEKA CORP

(22)Date of filing : 17.03.2008

(72)Inventor : OKAMOTO TOSHIHIKO
SAKAGUCHI MASAFUMI
YUKIMOTO SADA0
TAKASE JUNJI
WAKABAYASHI KATSUO
ANDO HIROSHI

(30)Priority

Priority number : 2001226971	Priority date : 27.07.2001	Priority country : JP
2001295770	27.09.2001	JP
2001340999	06.11.2001	JP

(54) CURABLE COMPOSITION

(57)Abstract:

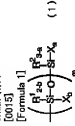
PROBLEM TO BE SOLVED: To provide a curable composition giving a cured material which ensures practical curability and recovery properties and has mechanical properties including high strength and high elongation.

SOLUTION: The curable composition comprises (A) an organic polymer having at least one silicon-containing group which has a hydroxy group or a hydrolyzable group bonded to the silicon atom and which is crosslinkable by forming siloxane bonds, and (B) one or more sorts of metal carboxylates selected from calcium carboxylate, vanadium carboxylate, iron carboxylate, titanium carboxylate, potassium carboxylate, barium carboxylate, manganese carboxylate, nickel carboxylate, cobalt carboxylate and zirconium carboxylate.

zirconium.

[0013] An amine compound is related with the aforementioned hardenability constituent which becomes as an essential ingredient as a (C) ingredient.

[0014] As a desirable embodiment, a number average molecular weight is within the limits of 500-50,000, and an organic polymer of the (A) ingredient is a general formula to an end and/or a side chain of a main chain (1):



[Formula 1]

[0015] (R¹ and R² among a formula) They are an alkyl group of the carbon numbers 1-20, an aryl group of the carbon numbers 6-20, an allyl group of the carbon numbers 7-20 or (R³)₃SiO independently, respectively. - (R) respectively - independent - the substitution of the carbon numbers 1-20, or an unsaturated hydrocarbon group - it is - it is the Tert ORGANO siloxy group atom. - a hydroxyl group or a hydroxyloxy salt independently, respectively, 1, 2, or 3 is 1, 2, or 3, and 2 and 3 are not simultaneously set to 0. The integer of n is 1, 2, or 3, and it is linked with a hardenability constituent given in said either having one or more hydroxyloxy silyl groups per molecule and/or.

[0016] It is related with the aforementioned hardenability constituent characterized by X being an alkoxy group as a desirable embodiment.

[0018] As a desirable embodiment, the organic polymer of the (A) ingredient is related with a hardenability constituent given in said either which is a polyoxyalkylene series polymer and/or a saturated hydrocarbon system polymer.

[0019] As a desirable embodiment, said saturated hydrocarbon system polymer is related with the aforementioned hardenability constituent which is a polymer having a repeating unit resulting from isobutylene 50% of the weight or more in a total amount.

[0020] As a desirable embodiment, a carboxylic acid zirconium of the (B) ingredient is related with a hardenability constituent given in said either which uses as the main ingredients carboxylic acid metal salt expressed with a general formula (12).

(12) (OCOR)₂ (12)

(The inside R of a formula is substitution or an unsubstituted hydrocarbon group, and may include a carbon carbon double bond.)

As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is the carboxylic acid metal salt in which the melting point has an acid radical of carboxylic acid which is 65 ° or less.

As a desirable embodiment, a carbon number in which carboxylic acid metal salt of the (B) ingredient contains a carboxyl group is related with a hardenability constituent given in said either which is a carbon number in which the carboxylic acid metal salt which has an acid radical of carboxylic acid which is 2-17.

As a desirable embodiment, carboxylic acid metal salt of the (B) ingredient is related with a hardenability constituent given in said either which is metal salt of a carboxylic acid group content compound chosen from octyloic acid, 2-ethylhexanoic acid, n-octanoic acid, oleic acid, or

naphthenic acid.

[0023] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient to (A) ingredient 100 weight section as a desirable embodiment.

[0024] It is related with a hardenability constituent given in said either containing the (B) ingredient of a quantity which serves as 0.005 - 5 weight section by metallic element conversion contained in the (B) ingredient, the (C) ingredient 0.01 - 20 weight sections to (A) ingredient 100 weight section as a desirable embodiment.

[0025] The mode of Carrying Out the Invention

Hereafter, this invention is explained in detail.

[0026] Restriction in particular does not have a principal chain skeleton of an organic polymer which has a reactive silicon group used for the invention, and it can use a thing with various kinds of principal chain skeletons.

[0027] Specifically A polyoxyethylene, polyoxypropylene, polyoxy butylene, Polyoxy tetramethylene, a polyoxyethylene polyoxypropylene copolymer, Or polyoxyalkylene series polymers, such as a polyoxyethylene polyoxypropylene, polyoxybutylene, An ethylene-propylene system copolymer. The copolymer of polyisobutylene, isobutylene, isoprene, etc., polyisoprene. A copolymer with polyisoprene, isoprene or butadiene, acrylonitrile, styrene, etc. Hydrocarbon system polymers, such as polyethylene, polyolefin, polyethylene system polymer produced by hydrogenating polyolefins or these as a hydrocarbon system polymer. Condensation with dibasic acid, such as adipic acid, and glycol. Or the polyester system polymer obtained by the ring opening polymerization of lactone: The polyuretic ester produced by carrying out the radical polymerization of the monomers, such as ethyl acrylate and butyl acrylate, Vinyl-based polymers, such as an acrylic ester system copolymer with acrylic ester, such as ethyl acrylate and butyl acrylate, vinyl acetate, acrylonitrile, methyl methacrylate, styrene, etc. A vinyl polymer. Nylon 610 by the condensation polymerization of the nylon 6 by the ring opening polymerization of epsilon caprolactam, hexamethylenediamine, Nylon 66 by the condensation polymerization of adipic acid and hexamethylenediamine, and abasic acid. Nylon 11 by the condensation polymerization of epsilon-aminoundecanoic acid. Condensation polymerization is carried out from polyamide system polymer, for example, bisphenol A, and the carbonyl chlorides which have a two or more-ingredient ingredient among Nylon 12 by the ring opening polymerization of epsilon-amine RAURO lactam, and the above-mentioned nylon, such as copolyamide. The polycarbonate system polymer manufactured, a diallyl phthalate system polymer etc., are illustrated.

[0028] Since acquisition and manufacture are easy among polymers with the above-mentioned principal chain skeleton, a polyoxyalkylene series polymer, a hydrocarbon system polymer, a polyester system polymer, a vinyl system copolymer, a polycarbonate system polymer, etc. are preferred. A saturated hydrocarbon system copolymer, and a polyoxyalkylene series polymer and a vinyl system copolymer have a comparatively low glass transition temperature, and their hardened material obtained is especially preferred from excellent in cold resistance.

[0029] As a saturated hydrocarbon system polymer which has a reactive silicon group used for this invention, the reactive silicon group content saturated hydrocarbon system polymer obtained from saturated hydrocarbon system polymers, such as polyisobutylene, hydrogenated polybutadiene, and polyisoprene polyisopren, is related.

[0030] The reactive silicon group contained in the organic polymer which has a reactive silicon group is a basis which can construct a bridge by formation of the siloxane bond which is a reaction which has the hydroxyl group or hydroxyloxy basis combined with the silicon atom, and is accelerated with the carboxylic acid metal salt which is the (B) ingredient.

実施例	組成	重量部	成分	重量部
(A) 100	PS-32	100	PS-32	100
(B) 100	PS-32	100	PS-32	100
(C) 100	PS-32	100	PS-32	100
(D) 100	PS-32	100	PS-32	100
(E) 100	PS-32	100	PS-32	100
(F) 100	PS-32	100	PS-32	100
(G) 100	PS-32	100	PS-32	100
(H) 100	PS-32	100	PS-32	100
(I) 100	PS-32	100	PS-32	100
(J) 100	PS-32	100	PS-32	100
(K) 100	PS-32	100	PS-32	100
(L) 100	PS-32	100	PS-32	100
(M) 100	PS-32	100	PS-32	100
(N) 100	PS-32	100	PS-32	100
(O) 100	PS-32	100	PS-32	100
(P) 100	PS-32	100	PS-32	100
(Q) 100	PS-32	100	PS-32	100
(R) 100	PS-32	100	PS-32	100
(S) 100	PS-32	100	PS-32	100
(T) 100	PS-32	100	PS-32	100
(U) 100	PS-32	100	PS-32	100
(V) 100	PS-32	100	PS-32	100
(W) 100	PS-32	100	PS-32	100
(X) 100	PS-32	100	PS-32	100
(Y) 100	PS-32	100	PS-32	100
(Z) 100	PS-32	100	PS-32	100

[0157]

As opposed to the polyester system polymer which serves as the (A) ingredient of this invention in working example 5, (B) By using the lauryl amine which acts the carboxylic acid zincium salt which acts as a co-catalyst as a (C) ingredient further as a silanol condensation catalyst as an ingredient. Although hardenability was slightly inferior as compared with the comparative example 2 using diisobutyl tin diacetate as a tetravalent tin catalyst, almost comparable elongation and an adhesive property were revealed and it checked that 1 liquid mold-curing nature constituent which may be sufficient for practical use was obtained (Table 2).

[0158]

(Synthetic example 1)

Use polyoxymethylene triol of the molecular weight 3,000 [about 3 as an initiator, and propylene oxide is polymerized in a zinc acetate catalyst, and propylene oxide is polymerized in a zinc acetate catalyst. Number average molecular weight 26,000 polyoxymethylene triol in which the column measured by GPC method using THF using the TOSOH TSK-GEL H type using TOSOH HLC-H120GPC as a liquid-sending system) polypropylene oxide was obtained. Then, the methanol solution of NaOMe of the equivalent was added 1.2 times to the hydroxyl group and polypropylene oxide, and methanol was distilled off, and also the allyl chloride was added, and the hydroxyl group of the end was changed into the allyl group. By the above, the end obtained 3 organic-functions polypropylene oxide of the number average molecular weight 26,000 [about 1 which is an allyl group.

[0159]

The nitrogen purge was carried out, after having added 500 g of allyl and 3 organic-functions polypropylene oxide and 10 g of hexane which were obtained above to 1L autoclave, dehydrating azeotropically at 90 ° and distilling off hexane under decompression. On the other hand, after adding 30microl of platinum divinyl disiloxane complex (it is 3% of the weight of xylene solution by platinum conversion) 1.70 g of dimethoxymethylsilane was dropped. After making the mixed solution react at 90 ° for 2 hours, unreacted dimethoxymethylsilane was distilled off under decompression and the reactive silicon group content polyoxymethylene series polymer (A-1) was obtained. The number average molecular weight of the obtained polymer (A-1) was about 26,000. The allyl group introduction rate was measured by the following methods by ¹H-NMR (it measures in a CDCl₃ solvent using JEOL JNM-LA-400).

[0160]

Receiving the peak integral value of CH₃ group (near 1.2 ppm) of the polypropylene oxide main chain of said allyl and 3 organic-functions polypropylene oxide before a hydroxylation reaction. Relative value of the peak integral value of an allyl and proton (near CH₂-CH=CH₂-5.1 ppm) : <2>. Receive the peak integral value of CH₃ group (near 1.2 ppm) of the polypropylene oxide main chain of the allyl

and polypropylene oxide (A-1) after a hydroxylation reaction. Relative-value: <2> of the peak integral value of the proton (near CH₃(CH₂O)₂-CH₂-CH₂-0.8 ppm) of the methylene group combined with the silicon atom of the end allyl group to the allyl group introduction rate (<2>/<1>) was 78%.

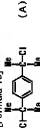
[0161]

(Synthetic example 2)

After attaching a three-way cock to the resisting pressure glass container of 2L and carrying out the nitrogen purge of the inside of a container to it. Using an injector, in a container 262.5 ml of ethylohexadecane (thing dry by neglecting 1 or more night with the molecular sieves 3A), and 187.5 ml of toluene (thing dry by neglecting 1 or more night with the molecular sieves 3A), p-DQO (the following compound (A)) 4.85g (2.0mmol) was added.

[0162]

(Formula 10)



[0163]

Next, the resisting pressure glass extraction pipe with a needle valve containing 438 ml (515 mol) of isobutylene monomers was connected to the three-way cock, and after attaching the polymerization vessel all over dry ice / ethanol bus of -70 ° and cooling, the inside of a container was made decompression using the vacuum pump. After opening the needle valve and introducing an isobutylene monomer in a polymerization vessel from a liquefied gas extraction pipe, the inside of a container was returned to ordinary pressure by introducing nitrogen from one side in a three-way cock. Next, 0.72 g (0.7mmol) of 2-methylpyridine was added. Next, 10.55 ml (96.5mmol) of titanium tetrachloride was added, and the polymerization was started. 70 minutes after the polymerization start, 7.20 g (63.0mmol) of allyl trimethylsilane was added, and the introduction reaction of the allyl group was performed to molecular chain terminals. After adding allyl trimethylsilane and 200 ml of water washed [120 minutes] the reaction solution 4 times, the allyl end isobutylene system polymer was obtained by distilling off a solvent.

[0164]

Subsequently, the allyl and isobutylene system polymer 200g obtained in this way, the paraffin-base process of the (Jemiusu Kusan mako), which is a hydrocarbon system plasticizer. After mixing a scale name Diana process PS-32 100g and carrying out to temperature up to about 75 °, the 7.5x10³ equivalent was added [methyl dimethoxysilane] for 2.4 eq and a platinum (vinyl siloxane) complex to the allyl group of an end to the allyl group of an end, and the hydroxylation reaction was performed. FT-IR (Shimadzu IR-405) performed reaction product, and the absorption band on the olefin of 1640 cm⁻¹ disappeared in about 20 hours.

[0165]

2/1 of PS-32 which is the isobutylene system polymer and plasticizer which have a reactive silicon group in the both ends of the target chain of the mixtures (A-2) of the weight ratio were obtained. In this way, if the obtained polymer is measured by the GPC method (it was considered as the liquid-sending system and, as for the solvent, the column used CHCl₃ using Stokes K-804 using LC Model) made from Waters). The number average molecular weight was 17,600 and Mw/Mn (ratio of weight average molecular weight to a number average molecular weight) was 1.23. ¹H-NMR (using Varian Gemini300) The proton which belongs to each structure by measurement in CDCl₃ (the proton of initiator origin: 6.5-7.5 ppm) The methyl proton combined with the silicon atom of polymer-terminal origin: As a result of measuring and measuring the intensity of 0.0-0.1 ppm and the resonance signal of methoxy proton 3.4 - 3.5, the end allyl functional group number Fn (number of the allyl group per one molecule of isobutylene polymer) was 1.76.

[0167]

(Working example 6-15, comparative example 3)

(A) As an ingredient, various additive agents were measured, respectively, and it often headed with a

3 paint roll according to the formula shown in Table 2, using the reactive silicon group content polyoxysilylene series polymer (A-1) obtained in the synthetic example 1, and was considered as base resin.

[0166]

Next, as a (B) ingredient which is a silyl condensation catalyst, lauryl amine was further measured for the various carboxylic acid metal salt shown in Table 1 to the above-mentioned base resin as a (C) ingredient, the spatula was used for it, and it stirred and mixed for 3 minutes. It was made for all the numbers of mole of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0167]

The mold, about 3 mm thick and filled up with the spatula after mixing, and care of health on 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700, 710, 720, 730, 740, 750, 760, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 870, 880, 890, 900, 910, 920, 930, 940, 950, 960, 970, 980, 990, 1000, 1010, 1020, 1030, 1040, 1050, 1060, 1070, 1080, 1090, 1100, 1110, 1120, 1130, 1140, 1150, 1160, 1170, 1180, 1190, 1200, 1210, 1220, 1230, 1240, 1250, 1260, 1270, 1280, 1290, 1300, 1310, 1320, 1330, 1340, 1350, 1360, 1370, 1380, 1390, 1400, 1410, 1420, 1430, 1440, 1450, 1460, 1470, 1480, 1490, 1500, 1510, 1520, 1530, 1540, 1550, 1560, 1570, 1580, 1590, 1600, 1610, 1620, 1630, 1640, 1650, 1660, 1670, 1680, 1690, 1700, 1710, 1720, 1730, 1740, 1750, 1760, 1770, 1780, 1790, 1800, 1810, 1820, 1830, 1840, 1850, 1860, 1870, 1880, 1890, 1900, 1910, 1920, 1930, 1940, 1950, 1960, 1970, 1980, 1990, 2000, 2010, 2020, 2030, 2040, 2050, 2060, 2070, 2080, 2090, 2100, 2110, 2120, 2130, 2140, 2150, 2160, 2170, 2180, 2190, 2200, 2210, 2220, 2230, 2240, 2250, 2260, 2270, 2280, 2290, 2300, 2310, 2320, 2330, 2340, 2350, 2360, 2370, 2380, 2390, 2400, 2410, 2420, 2430, 2440, 2450, 2460, 2470, 2480, 2490, 2500, 2510, 2520, 2530, 2540, 2550, 2560, 2570, 2580, 2590, 2600, 2610, 2620, 2630, 2640, 2650, 2660, 2670, 2680, 2690, 2700, 2710, 2720, 2730, 2740, 2750, 2760, 2770, 2780, 2790, 2800, 2810, 2820, 2830, 2840, 2850, 2860, 2870, 2880, 2890, 2900, 2910, 2920, 2930, 2940, 2950, 2960, 2970, 2980, 2990, 3000, 3010, 3020, 3030, 3040, 3050, 3060, 3070, 3080, 3090, 3100, 3110, 3120, 3130, 3140, 3150, 3160, 3170, 3180, 3190, 3200, 3210, 3220, 3230, 3240, 3250, 3260, 3270, 3280, 3290, 3300, 3310, 3320, 3330, 3340, 3350, 3360, 3370, 3380, 3390, 3400, 3410, 3420, 3430, 3440, 3450, 3460, 3470, 3480, 3490, 3500, 3510, 3520, 3530, 3540, 3550, 3560, 3570, 3580, 3590, 3600, 3610, 3620, 3630, 3640, 3650, 3660, 3670, 3680, 3690, 3700, 3710, 3720, 3730, 3740, 3750, 3760, 3770, 3780, 3790, 3800, 3810, 3820, 3830, 3840, 3850, 3860, 3870, 3880, 3890, 3900, 3910, 3920, 3930, 3940, 3950, 3960, 3970, 3980, 3990, 4000, 4010, 4020, 4030, 4040, 4050, 4060, 4070, 4080, 4090, 4100, 4110, 4120, 4130, 4140, 4150, 4160, 4170, 4180, 4190, 4200, 4210, 4220, 4230, 4240, 4250, 4260, 4270, 4280, 4290, 4300, 4310, 4320, 4330, 4340, 4350, 4360, 4370, 4380, 4390, 4400, 4410, 4420, 4430, 4440, 4450, 4460, 4470, 4480, 4490, 4500, 4510, 4520, 4530, 4540, 4550, 4560, 4570, 4580, 4590, 4600, 4610, 4620, 4630, 4640, 4650, 4660, 4670, 4680, 4690, 4700, 4710, 4720, 4730, 4740, 4750, 4760, 4770, 4780, 4790, 4800, 4810, 4820, 4830, 4840, 4850, 4860, 4870, 4880, 4890, 4900, 4910, 4920, 4930, 4940, 4950, 4960, 4970, 4980, 4990, 5000, 5010, 5020, 5030, 5040, 5050, 5060, 5070, 5080, 5090, 5100, 5110, 5120, 5130, 5140, 5150, 5160, 5170, 5180, 5190, 5200, 5210, 5220, 5230, 5240, 5250, 5260, 5270, 5280, 5290, 5300, 5310, 5320, 5330, 5340, 5350, 5360, 5370, 5380, 5390, 5400, 5410, 5420, 5430, 5440, 5450, 5460, 5470, 5480, 5490, 5500, 5510, 5520, 5530, 5540, 5550, 5560, 5570, 5580, 5590, 5600, 5610, 5620, 5630, 5640, 5650, 5660, 5670, 5680, 5690, 5700, 5710, 5720, 5730, 5740, 5750, 5760, 5770, 5780, 5790, 5800, 5810, 5820, 5830, 5840, 5850, 5860, 5870, 5880, 5890, 5900, 5910, 5920, 5930, 5940, 5950, 5960, 5970, 5980, 5990, 6000, 6010, 6020, 6030, 6040, 6050, 6060, 6070, 6080, 6090, 6100, 6110, 6120, 6130, 6140, 6150, 6160, 6170, 6180, 6190, 6200, 6210, 6220, 6230, 6240, 6250, 6260, 6270, 6280, 6290, 6300, 6310, 6320, 6330, 6340, 6350, 6360, 6370, 6380, 6390, 6400, 6410, 6420, 6430, 6440, 6450, 6460, 6470, 6480, 6490, 6500, 6510, 6520, 6530, 6540, 6550, 6560, 6570, 6580, 6590, 6600, 6610, 6620, 6630, 6640, 6650, 6660, 6670, 6680, 6690, 6700, 6710, 6720, 6730, 6740, 6750, 6760, 6770, 6780, 6790, 6800, 6810, 6820, 6830, 6840, 6850, 6860, 6870, 6880, 6890, 6900, 6910, 6920, 6930, 6940, 6950, 6960, 6970, 6980, 6990, 7000, 7010, 7020, 7030, 7040, 7050, 7060, 7070, 7080, 7090, 7100, 7110, 7120, 7130, 7140, 7150, 7160, 7170, 7180, 7190, 7200, 7210, 7220, 7230, 7240, 7250, 7260, 7270, 7280, 7290, 7300, 7310, 7320, 7330, 7340, 7350, 7360, 7370, 7380, 7390, 7400, 7410, 7420, 7430, 7440, 7450, 7460, 7470, 7480, 7490, 7500, 7510, 7520, 7530, 7540, 7550, 7560, 7570, 7580, 7590, 7600, 7610, 7620, 7630, 7640, 7650, 7660, 7670, 7680, 7690, 7700, 7710, 7720, 7730, 7740, 7750, 7760, 7770, 7780, 7790, 7800, 7810, 7820, 7830, 7840, 7850, 7860, 7870, 7880, 7890, 7900, 7910, 7920, 7930, 7940, 7950, 7960, 7970, 7980, 7990, 8000, 8010, 8020, 8030, 8040, 8050, 8060, 8070, 8080, 8090, 8100, 8110, 8120, 8130, 8140, 8150, 8160, 8170, 8180, 8190, 8200, 8210, 8220, 8230, 8240, 8250, 8260, 8270, 8280, 8290, 8300, 8310, 8320, 8330, 8340, 8350, 8360, 8370, 8380, 8390, 8400, 8410, 8420, 8430, 8440, 8450, 8460, 8470, 8480, 8490, 8500, 8510, 8520, 8530, 8540, 8550, 8560, 8570, 8580, 8590, 8600, 8610, 8620, 8630, 8640, 8650, 8660, 8670, 8680, 8690, 8700, 8710, 8720, 8730, 8740, 8750, 8760, 8770, 8780, 8790, 8800, 8810, 8820, 8830, 8840, 8850, 8860, 8870, 8880, 8890, 8900, 8910, 8920, 8930, 8940, 8950, 8960, 8970, 8980, 8990, 9000, 9010, 9020, 9030, 9040, 9050, 9060, 9070, 9080, 9090, 9100, 9110, 9120, 9130, 9140, 9150, 9160, 9170, 9180, 9190, 9200, 9210, 9220, 9230, 9240, 9250, 9260, 9270, 9280, 9290, 9300, 9310, 9320, 9330, 9340, 9350, 9360, 9370, 9380, 9390, 9400, 9410, 9420, 9430, 9440, 9450, 9460, 9470, 9480, 9490, 9500, 9510, 9520, 9530, 9540, 9550, 9560, 9570, 9580, 9590, 9600, 9610, 9620, 9630, 9640, 9650, 9660, 9670, 9680, 9690, 9700, 9710, 9720, 9730, 9740, 9750, 9760, 9770, 9780, 9790, 9800, 9810, 9820, 9830, 9840, 9850, 9860, 9870, 9880, 9890, 9900, 9910, 9920, 9930, 9940, 9950, 9960, 9970, 9980, 9990, 10000, 10010, 10020, 10030, 10040, 10050, 10060, 10070, 10080, 10090, 10100, 10110, 10120, 10130, 10140, 10150, 10160, 10170, 10180, 10190, 10200, 10210, 10220, 10230, 10240, 10250, 10260, 10270, 10280, 10290, 10300, 10310, 10320, 10330, 10340, 10350, 10360, 10370, 10380, 10390, 10400, 10410, 10420, 10430, 10440, 10450, 10460, 10470, 10480, 10490, 10500, 10510, 10520, 10530, 10540, 10550, 10560, 10570, 10580, 10590, 10600, 10610, 10620, 10630, 10640, 10650, 10660, 10670, 10680, 10690, 10700, 10710, 10720, 10730, 10740, 10750, 10760, 10770, 10780, 10790, 10800, 10810, 10820, 10830, 10840, 10850, 10860, 10870, 10880, 10890, 10900, 10910, 10920, 10930, 10940, 10950, 10960, 10970, 10980, 10990, 11000, 11010, 11020, 11030, 11040, 11050, 11060, 11070, 11080, 11090, 11100, 11110, 11120, 11130, 11140, 11150, 11160, 11170, 11180, 11190, 11200, 11210, 11220, 11230, 11240, 11250, 11260, 11270, 11280, 11290, 11300, 11310, 11320, 11330, 11340, 11350, 11360, 11370, 11380, 11390, 11400, 11410, 11420, 11430, 11440, 11450, 11460, 11470, 11480, 11490, 11500, 11510, 11520, 11530, 11540, 11550, 11560, 11570, 11580, 11590, 11600, 11610, 11620, 11630, 11640, 11650, 11660, 11670, 11680, 11690, 11700, 11710, 11720, 11730, 11740, 11750, 11760, 11770, 11780, 11790, 11800, 11810, 11820, 11830, 11840, 11850, 11860, 11870, 11880, 11890, 11900, 11910, 11920, 11930, 11940, 11950, 11960, 11970, 11980, 11990, 12000, 12010, 12020, 12030, 12040, 12050, 12060, 12070, 12080, 12090, 12100, 12110, 12120, 12130, 12140, 12150, 12160, 12170, 12180, 12190, 12200, 12210, 12220, 12230, 12240, 12250, 12260, 12270, 12280, 12290, 12300, 12310, 12320, 12330, 12340, 12350, 12360, 12370, 12380, 12390, 12400, 12410, 12420, 12430, 12440, 12450, 12460, 12470, 12480, 12490, 12500, 12510, 12520, 12530, 12540, 12550, 12560, 12570, 12580, 12590, 12600, 12610, 12620, 12630, 12640, 12650, 12660, 12670, 12680, 12690, 12700, 12710, 12720, 12730, 12740, 12750, 12760, 12770, 12780, 12790, 12800, 12810, 12820, 12830, 12840, 12850, 12860, 12870, 12880, 12890, 12900, 12910, 12920, 12930, 12940, 12950, 12960, 12970, 12980, 12990, 13000, 13010, 13020, 13030, 13040, 13050, 13060, 13070, 13080, 13090, 13100, 13110, 13120, 13130, 13140, 13150, 13160, 13170, 13180, 13190, 13200, 13210, 13220, 13230, 13240, 13250, 13260, 13270, 13280, 13290, 13300, 13310, 13320, 13330, 13340, 13350, 13360, 13370, 13380, 13390, 13400, 13410, 13420, 13430, 13440, 13450, 13460, 13470, 13480, 13490, 13500, 13510, 13520, 13530, 13540, 13550, 13560, 13570, 13580, 13590, 13600, 13610, 13620, 13630, 13640, 13650, 13660, 13670, 13680, 13690, 13700, 13710, 13720, 13730, 13740, 13750, 13760, 13770, 13780, 13790, 13800, 13810, 13820, 13830, 13840, 13850, 13860, 13870, 13880, 13890, 13900, 13910, 13920, 13930, 13940, 13950, 13960, 13970, 13980, 13990, 14000, 14010, 14020, 14030, 14040, 14050, 14060, 14070, 14080, 14090, 14100, 14110, 14120, 14130, 14140, 14150, 14160, 14170, 14180, 14190, 14200, 14210, 14220, 14230, 14240, 14250, 14260, 14270, 14280, 14290, 14300, 14310, 14320, 14330, 14340, 14350, 14360, 14370, 14380, 14390, 14400, 14410, 14420, 14430, 14440, 14450, 14460, 14470, 14480, 14490, 14500, 14510, 14520, 14530, 14540, 14550, 14560, 14570, 14580, 14590, 14600, 14610, 14620, 14630, 14640, 14650, 14660, 14670, 14680, 14690, 14700, 14710, 14720, 14730, 14740, 14750, 14760, 14770, 14780, 14790, 14800, 14810, 14820, 14830, 14840, 14850, 14860, 14870, 14880, 14890, 14900, 14910, 14920, 14930, 14940, 14950, 14960, 14970, 14980, 14990, 15000, 15010, 15020, 15030, 15040, 15050, 15060, 15070, 15080, 15090, 15100, 15110, 15120, 15130, 15140, 15150, 15160, 15170, 15180, 15190, 15200, 15210, 15220, 15230, 15240, 15250, 15260, 15270, 15280, 15290, 15300, 15310, 15320, 15330, 15340, 15350, 15360, 15370, 15380, 15390, 15400, 15410, 15420, 15430, 15440, 15450, 15460, 15470, 15480, 15490, 15500, 15510, 15520, 15530, 15540, 15550, 15560, 15570, 15580, 15590, 15600, 15610, 15620, 15630, 15640, 15650, 15660, 15670, 15680, 15690, 15700, 15710, 15720, 15730, 15740, 15750, 15760, 15770, 15780, 15790, 15800, 15810, 15820, 15830, 15840, 15850, 15860, 15870, 15880, 15890, 15900, 15910, 15920, 15930, 15940, 15950, 15960, 15970, 15980, 15990, 16000, 16010, 16020, 16030, 16040, 16050, 16060, 16070, 16080, 16090, 16100, 16110, 16120, 16130, 16140, 16150, 16160, 16170, 16180, 16190, 16200, 16210, 16220, 16230, 16240, 16250, 16260, 16270, 16280, 16290, 16300, 16310, 16320, 16330, 16340, 16350, 16360, 16370, 16380, 16390, 16400, 16410, 16420, 16430, 16440, 16450, 16460, 16470, 16480, 16490, 16500, 16510, 16520, 16530, 16540, 16550, 16560, 16570, 16580, 16590, 16600, 16610, 16620, 16630, 16640, 16650, 16660, 16670, 16680, 16690, 16700, 16710, 16720, 16730, 16740, 16750, 16760, 16770, 16780, 16790, 16800, 16810, 16820, 16830, 16840, 16850, 16860, 16870, 16880, 16890, 16900, 16910, 16920, 16930, 16940, 16950, 16960, 16970, 16980, 16990, 17000, 17010, 17020, 17030, 17040, 17050, 17060, 17070, 17080, 17090, 17100, 17110, 17120, 17130, 17140, 17150, 17160, 17170, 17180, 17190, 17200, 17210, 17220, 17230, 17240, 17250, 17260, 17270, 17280, 17290, 17300, 17310, 17320, 17330, 17340, 17350, 17360, 17370, 17380, 17390, 17400, 17410, 17420, 17430, 17440, 17450, 17460, 17470, 17480, 17490, 17500, 17510, 17520, 17530, 17540, 17550, 17560, 17570, 17580, 17590, 17600, 17610, 17620, 17630, 17640, 17650, 17660, 17670, 17680, 17690, 17700, 17710, 17720, 17730, 17740, 17750, 17760, 17770, 17780, 17790, 17800, 17810, 17820, 17830, 17840, 17850, 17860, 17870, 17880, 17890, 17900, 17910, 17920, 17930, 17940, 17950, 17960, 17970, 17980, 17990, 18000, 18010, 18020, 18030, 18040, 18050, 18060, 18070, 18080, 18090, 18100, 18110, 18120, 18130, 18140, 18150, 18160, 18170, 18180, 18190, 18200, 18210, 18220, 18230, 18240, 18250, 18260, 18270, 18280, 18290, 18300, 18310, 18320, 18330, 18340, 18350, 18360, 18370, 18380, 18390, 18400, 18410, 18420, 18430, 18440, 18450, 18460, 18470, 18480, 18490, 18500, 18510, 18520, 18530, 18540, 18550, 18560, 18570, 18580, 18590, 18600, 18610, 18620, 18630, 18640

Table 3, the value of Tb (breaking strength) and Eb (elongation after fracture) of hardened material physical properties is larger.
High elongation and high intensity were shown.

[0173]

(Working example 16-23, comparative example 4)

(A) Using the mixture (A-2) of the isobutylene system polymer and plasticizer which have as an ingredient the reactive silicon group obtained in the synthetic example 2, various additive agents were measured, respectively, and it often kneaded with a 3 paint roll according to the formula shown in Table 4, and was considered as base resin.

[0174]

Next, the various carboxylic acid metal salt shown in Table 4 as a (B) ingredient which is a silanol condensation catalyst was measured, and also as a (C) ingredient which is a curing agent was used together the above-mentioned (A) resin. The result of the measurement is shown in Table 4. In working example 16-28 and the comparative example 16-29, the hardened state was evaluated for 3 minutes to it. It was recuperated at 23 °C and the surface hardened state was evaluated five days afterward. It was made for all the numbers of mole of the metal atom containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become the same here.

[0175]

The evaluation result of the hardened state five days after the combination presentation of base resin, a curing catalyst, etc. is shown in Table 4. What the surface had hardened O in front for five days afterward is shown, and it is shown that x had not hardened five days after.

[0176]

[Table 4]

成分名		配合割合 (重量部)										硬化状態 (5日後)	
成分名		1	2	3	4	5	6	7	8	9	10	硬化	未硬化
硬化剤 (B)	安息香酸メチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸エチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ブチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸オクチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ドデシル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ステアール	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ラウリン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸パルミチン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ミリスチン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸オレフィン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
硬化剤 (C)	安息香酸メチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸エチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ブチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸オクチル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ドデシル	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ステアール	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ラウリン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸パルミチン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸ミリスチン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○
	安息香酸オレフィン	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	○	○

[0177]

When the various carboxylic acid metal salt of working example 16-28 is used as shown in Table 4, in spite of having used the silicon condensation catalyst of this non-in series, the surface has hardened in five days.

Practical hardenability was shown.

On the other hand, when the carboxylic acid zinc of the comparative example 4 was used, hardenability had not hardened five days after bad.

[0178]

As mentioned above, the organic polymer which has at least one reactive silicon group in the (A) molecule, (B) Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, carboxylic acid titanium, carboxylic acid cobalt, carboxylic acid nickel, carboxylic acid zinc, carboxylic acid aluminum, carboxylic acid chromium, and carboxylic acid metal salt chosen from the carboxylic acid carboxylic acid zirconium and a hardenability [see others] constituent. In spite of being a non-in series catalyst, practical hardenability is shown, and it turns out that hardened material physical properties are also fitness (high elongation and high intensity).

[0179]

(Constituent using the trimethoxysilyl group as a reactive silicon group)

If a trimethoxysilyl group uses the polyoxalkylene series polymer which exists in molecular chain terminals as a reactive silicon group, a cure rate will become large from the polymer of the synthetic example 1. The direction of a trimethoxysilyl group of this is because reactivity is larger than a methyl dimethoxy silyl group. Such a polymer is indicated to JP-H11-12480A or JP-2001-72855A. For example, the same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1 of manufacture of JP-H11-12480A. The tack free time of this constituent is shorter than working example 6-15.

[0180]

The same hardenability constituent as working example 6-15 can be prepared using the polymer indicated for the example 1-4 of manufacture of JP-2001-72855A. The tack free time of this constituent is shorter than working example 6-15. Therefore, a catalyst amount can be lessened, if cure time is made into the same grade and the polymer which has the above-mentioned trimethoxysilyl group will be used.

[0181]

The mixture of the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxy silyl group is used as a polymer, cure time and the physical properties of a hardened material are freely controllable. For example, the hardenability constituent of working example 6-15 can be prepared using the polymer which mixed the polymer which has a trimethoxysilyl group, and the polymer which has a methyl dimethoxy silyl group by the weight ratio of 1:10-10:1.

[0182]

Working example when the polymer which has a trimethoxysilyl group is used is shown below.

[0183]

(Synthetic bottom 3)
The trade of bottom of N_2 atmosphere 1L autoclave. According to a composite metal complex compound catalyst, it polymerizes. The obtained polypropylene oxide. Use and to the compound number average molecular weight 17,000 and the polypropylene diol 1000g of molecular weight-distribution Mw/Mn=1.20 as 19g of gamma-isocyanate propylmethacrylate (Nippon Sanco make Y-5187), and a catalyst, 0.05 g of dibutyl tin screw isocyanate/thioglycolates (made in [U-360] transformation [Japanese east 3]) is added. It reacted at 90 °+ until the isocyanate group was no longer detected in IR under the nitrogen air current. In this, and the reactive silicon group content polyoxpropylene (A-3) by which the trimethoxysilyl group was introduced into about 80% of ends was obtained.

[0184]

(Working example 29-32)

(A) The polyoxalkylene series polymer (A-1) which has as an ingredient the methyl dimethoxy silyl group obtained in the synthetic example 1. The various carboxylic acid metal salt which is the (B) ingredients according to the formula shown in Table 5 using the polyoxalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3, (C) Lauryl amine which is an

ingredient was measured, respectively, the spatula was used, and it stirred and mixed for 30 seconds. It was made for all the numbers of mols of the (B) ingredient containing the number of addition parts of the various carboxylic acid metal salt of the (B) ingredient to become almost the same here. The surface was lightly pressed down with the spatula after mixing, and time (sealer-covered time) until a constituent stops adhering at the tip of a spatula was measured. An evaluation result is shown in Table 5.

Table 5.

[0185]

[Table 5]

組成 (重量部)		硬化時間			
(A) 成分	A-1	29	30	31	32
ニメチルジメトキシシリルポリオキシプロピレン (9)	日本化学工業 (株)	100	100	100	100
(B) 成分	ニメチルジメトキシシリルポリオキシプロピレン (9)	5.6	6.1	5.6	5.6
(C) 成分	ラウリルアミン	0.05	0.05	0.05	0.05
反応温度 (32℃)	45分	21分	20分	20分	18分

(D) 2-エチルヘキサン酸のメタノール溶液、全量 (5 g) 全量: 8 %

(E) 2-エチルヘキサン酸のメタノール溶液、全量 (5 g) 全量: 5 %

[0186]

As shown in Table 5, the polyoxalkylene series polymer (A-3, working example 30 and 32) which has a trimethoxysilyl group had the cure rate quicker than the polyoxalkylene series polymer (A-1: working example 29 and 31) which has a methyl dimethoxy silyl group.

[0187]

The same hardenability constituent as working example 6-15 can be prepared using the polyoxalkylene series polymer (A-3) which has the trimethoxysilyl group obtained in the synthetic example 3. The tack free time of this constituent has short cure time, and good physical properties are acquired.

[0188]

(Constituent which used the epoxy resin together)

The same hardenability constituent as working example 6-15 can be prepared using the constituent which used the epoxy resin together with the constituent using organic polymer and an epoxy resin. When this constituent is used, the manifestation of adhesive strength is quick.

[0189]

(A) The organic polymer which has the hydroxyl group or hydrolytic basis combined with the silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond. (B) Carboxylic acid calcium, carboxylic acid vanadium, carboxylic acid iron, Carboxylic acid titanium, carboxylic acid potassium, carboxylic acid barium. The hardenability constituent containing one or more sorts of carboxylic acid metal salt which it comes to choose out of carboxylic acid manganese, carboxylic acid nickel, carboxylic acid cobalt, and a carboxylic acid zirconium. While revealing practical hardenability and stability, the hardened material obtained shows the outstanding mechanical physical property which has high intensity and high elongation as compared with the case where the carboxylic acid tin currently used conventionally is used as a curing catalyst. Therefore, the hardenability constituent of this invention is very useful as a elastomer, such as a sealing material, adhesives, a binder.

[Translation done.]